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TECHNOLOGY CENTER

INVESTIGATION OF SINGLE ENERGY GAP SOLAR CELL MATERIAL

Contract No. DA36-039-SC-85247

Robert J. Robinson

U. S. Army Signal Research and Development Laboratory
Ft. Monmouth, New Jersey

ARMOUR RESEARCH FOUNDATION

of
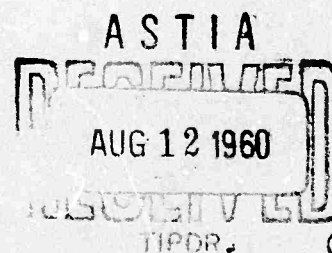
Illinois Institute of Technology
Technology Center
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Period Report No. 2

Covering the period of January 1, 1960 to June 30, 1960.

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ABSTRACT

The purpose of this program is to develop, if possible, a single gap solar cell material which lends the possibility of lower production cost, increased practical efficiency and better high temperature characteristics than can be expected from silicon. Cadmium telluride, the material chosen for the study, is a comparatively new material in semiconductor technology, and the principal emphasis in this program is on crystal growth. During the second period, dense, nearly single crystal ampoules have been made with resistivities ranging between one ohm cm and 10^6ohm cm depending upon the dopant concentration. However, considerable work remains to increase the carrier lifetimes in the low resistivity material, and to obtain better uniformity throughout the ampoule. A controlled atmosphere zone refining furnace is currently being calibrated for this purpose.

Solar cell fabrication experiments were carried out in order to evaluate the currently available material from the standpoint of solar cell applications. In part, the purpose was to determine how the material behaved under a fabrication cycle. Pitting during heat treatment, and lack of wide area photovoltaic response on the treated material indicated inhomogeneity in the samples with a resulting compensation cancelling or shorting of the photovoltaic emf.

Thermoelectric probe measurements on treated and untreated samples showed the anticipated inhomogeneities which were evidenced by alternate n and p-type regions on the surface. In addition, the pitting appears

associated with p-type regions. Very recently a low resistivity ampoule has become available which does not show the alternate n and p-type inhomogeneities, and, in addition, probe photovoltages in the 0.6 volt region are observed.

INVESTIGATION OF SINGLE ENERGY GAP SOLAR CELL MATERIAL

I.   INTRODUCTION

A program on the "Investigation of Single Energy Gap Solar Cell Material" under Contract No. DA36-039-SC-85247 was begun on September 1, 1959 and extends to August 31, 1960. The purpose of the program is to develop, if possible, a single gap solar cell material which lends the possibility of lower production cost, increased practical efficiency and better high temperature characteristics than can be expected from silicon. Further, the single gap material to be investigated is cadmium telluride in both single crystal and thin layer form with emphasis on a single crystal converter. This is a Periodic Report No. 2 covering the period January 1, 1960 to June 30, 1960.

Cadmium telluride (CdTe) is a Group II-Group VI compound with a band gap of 1.4 electron volts (ev.). It is a particularly interesting member of this class, however, because both p-type and n-type material can be made and p-n junctions formed. In fact, it is the combination of a favorable band gap, and the possibility of p-n junction formation which makes this material of interest as a higher-than-ambient temperature solar cell.

Work on crystal growth and on the properties of CdTe, though, has been limited compared to silicon and the better known Group III-Group V compounds. During this second period, as in the first, the principal emphasis has been on the preparation of good single crystals. To date considerable

progress has been made. The most recent ampoules have been dense, nearly single crystal, with a resistivity in the one ohm cm region. The problem of porosity in the ampoules and low mechanical strength, even in material doped with indium at a 0. 1 mol percent, appears to have been surmounted. However, considerable work still remains on making material with better lifetimes, and better uniformity from a semiconductor viewpoint. A zone refiner is currently being developed for growing the crystals under a controlled atmosphere which should lead to this better material.

II.   SINGLE CRYSTAL CADMIUM TELLURIDE

The method for growing single crystal CdTe involves (1) combination of the elemental components in stoichiometric proportions, (2) reaction of the elements at elevated temperatures under conditions designed to prevent decomposition of the desired compound, and (3) growth of a single crystal by the Stockbarger technique.

The first crystals prepared in this laboratory were characterized by a high degree of distortion crystallization probably induced by the blowholes in the matrix. As better control over stoichiometry was obtained and as the growth conditions were refined, the porosity of the crystals was reduced. This was accompanied by an increase in the size of the single crystal domains. Eventually single crystals were obtained of approximately one cm diameter which were completely free of any macroscopic porosity.

The boules currently being grown are dense, approach single

crystal, and have resistivities from one ohm cm to 10^{6} ohm cm depending upon the dopant concentration. The techniques and problems of growing cadmium telluride, as well as the direction of the future work, is discussed in Appendix I.

III. SOLAR CELL FABRICATION STUDIES

Solar cell fabrication experiments were carried out on presently available cadmium telluride in order to evaluate it from the standpoint of solar cell application even though it was known that the material was not completely single crystal, and that inhomogeneities existed in the samples. In part, the purpose was to determine how the material behaved during a fabrication cycle. The n-type cadmium telluride grown at Armour Research Foundation was compared with material obtained from Semi-Elements, Incorporated. While the inhomogeneities were apparently responsible for the poor wide area photovoltaic response, it was evident that progress in cadmium telluride has been obtained. Very recently a sample of dense, n-type cadmium telluride has been obtained which evidences much less inhomogeneity. While the work on this sample is preliminary, 0.6 volt photovoltages have been observed. This work is discussed in Appendix II.

IV. THERMOELECTRIC PROBE MEASUREMENTS

The solar cell fabrication experiments described previously led to two conclusions which suggested marked inhomogeneity in the samples.

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It was decided to make a device which would permit small area probing for n and p-type regions. The anticipated inhomogeneities were found as indicated by alternate n and p-type regions across the same. The measurements were made on slices from different ampoules and a number of curves are shown in Appendix III. The pitting which occurred during the diffusion experiments appears to be associated with p-type regions, and the lack of wide area photovoltaic response appears to be due to compensations cancelling or short circuiting.

A very recent sample shows only n-type behavior with a nearly constant thermoelectric power, which indicate that better material is becoming available; and further it indicates that the thermoelectric probe is a useful monitoring device.

V. SUMMARY

Cadmium telluride is comparatively a new material in semiconductor technology, and the state of art is early compared to silicon and the better known Group III-Group V compounds. Progress has been made, however, in growing dense, nearly single ampoules with resistivities between one ohm cm and 10^6ohm cm using indium as dopant. Better lifetimes and greater uniformity from a semiconductor viewpoint are desired and work on a zone refining apparatus is currently in progress to handle this problem.

Solar cell fabrication studies on the currently available material have been made in order to determine how cadmium telluride behaves during

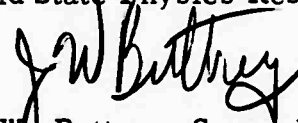ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

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the fabrication cycle. The lack of wide area photovoltaic response after fabrication, even though previous probe studies had indicated a photovoltage, and the tendency to pit during heat treatment indicated inhomogeneous materi- al. Thermoelectric probe measurements showed that the material was in- homogeneous with interspersed n and p-type regions. Very recently one ohm cm material has been grown showing only n-type regions on probing.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION
of Illinois Institute of Technology

Robert J. Robinson, Research Physicist
Solid State Physics Research

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Solid State Physics Research

APPROVED BY:

J. J. Brophy, Assistant Director
of Physics Research

Appendix I

on

PREPARATION OF CADMIUM TELLURIDE

by

S. Susman
G. Yamate

Appendix I
PREPARATION OF CADMIUM TELLURIDE

Up to now only a small number of publications have treated the CdTe system. Moreover, none of them have demonstrated the ability to prepare high quality, single crystal CdTe of controlled composition. Recently, de Nobel[1] has published a two part study of the "Phase Equilibria and Semiconducting Properties of CdTe" which is an exhaustive treatment of the problem. Much of the interpretation of the current results on this program are based on the data presented in de Nobel's paper.

The present method for preparing single crystal CdTe is based on techniques developed in this laboratory for other 2-6 compounds (particularly PbSe). This method involves (1) combination of the elemental components in stoichiometric proportions, (2) reaction of the elements at elevated temperatures under conditions designed to prevent decomposition of the desired compound, and (3) growth of a crystal by the Stockbarger technique. No additional purification steps have been introduced into this basic scheme in these preparations. All manipulations have been performed in vacuo or in a pre-purified nitrogen atmosphere to minimize contamination of the starting materials or the compound.

The elemental reactants for the preparation of CdTe are 99.999+%

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[1] de Nobel, D., Philips Res. Rept. 14, 361-99, 430-92 (1959).

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pure tellurium[*] and 99.999+% pure cadmium metal[**]   The preparation of

CdTe is hindered by the fact that, although the reaction between the elements

starts readily at 500° C, temperatures in excess of 800° C are required to get

complete reaction.   At such temperatures, however, CdTe tends to decom-

pose markedly and no homogeneous phase will be obtained if this decomposi-

tion is not repressed.

Several alternate procedures are available to prevent compound de-

composition.   CdTe can be prepared under a vapor pressure of one of its

components.   Then, by mass action, the equilibrium

$$CdTe_{(s)} = Cd_{(g)} + 1/2Te_{2(g)}$$
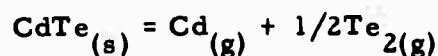
is driven to the left and decomposition is suppressed.   The reaction can also

be carried out under a pressure of inert gas.   Or, as a final alternate, the

reaction can be carried to completion in a volume of sufficiently small dead

space that little volume is available for extensive decomposition.   This latter

procedure has been used for the initial preparation of CdTe crystals.   How-

ever, it does not offer fine control over the composition of the crystal.   Only

by handling the CdTe crystal under definite pressure of the components is it

possible to exactly define the composition.

The container used for the preparation of CdTe and the subsequent

crystal growth is shown in Fig. 1.   The reaction chamber (C) is 25 mm fused

[*]   American Smelting and Refining Co. , Baltimore, Maryland.
[**]   The New Jersey Zinc Co. , Chicago, Illinois.

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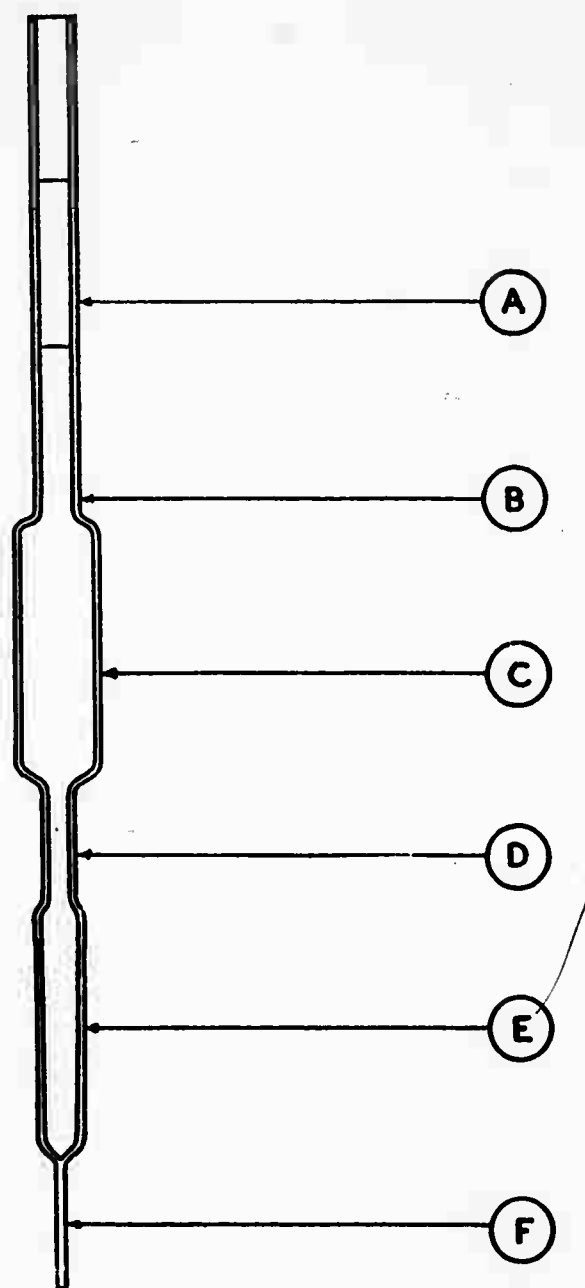
FIG. I. QUARTZ UNIT FOR PREPARATION OF
CdTe, AND GROWTH OF CdTe CRYSTALS.

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quartz and has attached to it, as an integral part, the 13 mm fused quartz ampoule (E) for crystal growth. The ampoule is drawn to a 60° cone and sealed to a quartz rod (F). This rod seats the ampoule in the support tube of the Stockbarger furnace and aligns the crystal on the axis of the furnace. The quartz unit is cleaned successively with detergent, a 50:50 mixture of conc. HNO_3 and 40% HF, a 50:50 mixture of conc. HNO_3 and H_2SO_4, and distilled water. It can then be sealed to a vacuum line through its graded seal (A) and outgassed at 900° C and 10-6 mm Hg for 16 hours.

The quartz unit is loaded with the reactants in a dry box pressurized above one atmosphere with prepurified nitrogen. Stoichiometric proportions of Cd and Te (calculated to yield a 25 - gram CdTe crystal) are weighed into the reaction chamber. The loaded unit is quickly transferred to the vacuum line, the pressure reduced to 10^{-5} mm Hg and a seal-off made at (B). Light heating with a torch serves to initiate the reaction between Cd and Te. The chamber and ampoule are soaked at 600° C for 30 min. and at 1100° C for one hour to complete the bulk of the reaction. The ampoule temperature is lowered while the chamber is maintained at 1100° C. This operation transfers the melt into the ampoule and also sublimes any unreacted Cd and Te into the ampoule. The ampoule is then slowly cooled to room temperature to prevent cracking. With the ampoule almost totally filled, it is sealed off at (D) leaving a dead space of ca. 5cc above the melt.

The Stockbarger furnace used to grow CdTe crystals embodies two auxiliary Kanthal heating coils fitted concentrically within a main Kanthal

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coil. The upper coil establishes the temperature zone required to melt the CdTe. Upon solidifying, the crystal passes into the botton zone established by the main coil. This permits crystal growth in a controlled temperature gradient followed by a slow, controlled annealing to room temperature.

The power input to the furnace is regulated by two saturable core reactors, one for the main coil and one for the auxiliary coils. Absolute temperature is controlled to $\pm 1°$ C (the minimum detectable deviation in the controller). By splitting the dc saturation to the main coil and the auxiliary coil, it is possible to establish temperature gradients of varying slope and to control the slopes to $\pm 0.1°$ C/cm. A traveling thermocouple in the ampoule holder records the temperature profile for each run.

Vertical traverse of the melt is obtained by a positive gear drive. By using interchangeable gear ratios, crystals can be grown at speeds varying from 10 cm to 1 mm per hour. CdTe crystals are currently being grown at 1 cm per hcur and 5 rpm. The crystals are 10 mm in diameter and up to 6 cm long.

Figure 2 is a photograph of the Stockbarger furnace and control panel prior to assembly of the support rod mechanism. Figure 3 presents a close-up view of the support rod assembly for lowering and rotating the a ampoule.

The crystals grown up to the present time have served to define a number of the important considerations in the preparation of single crystal CdTe of controlled composition. While the growth rate has been kept the
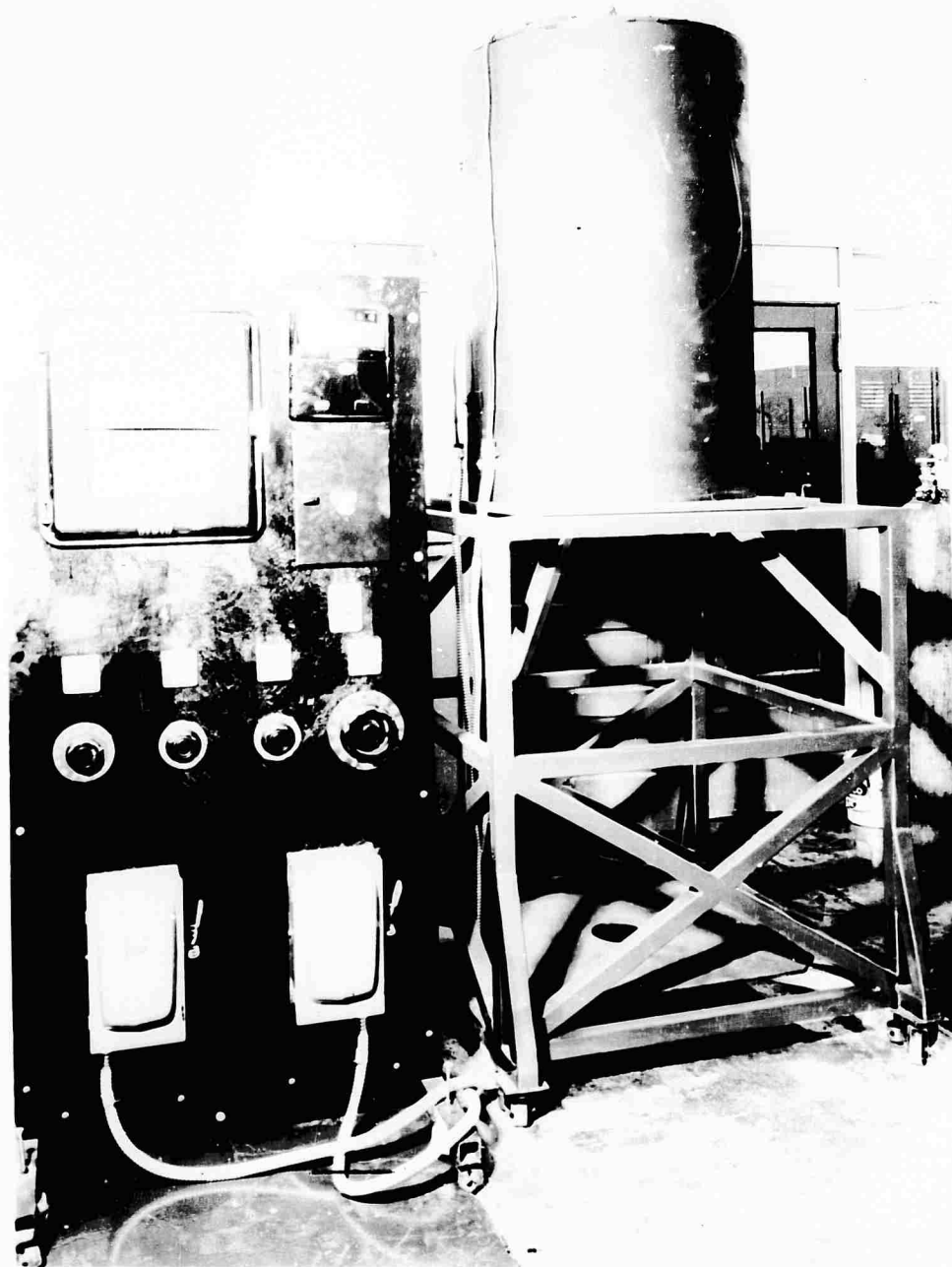
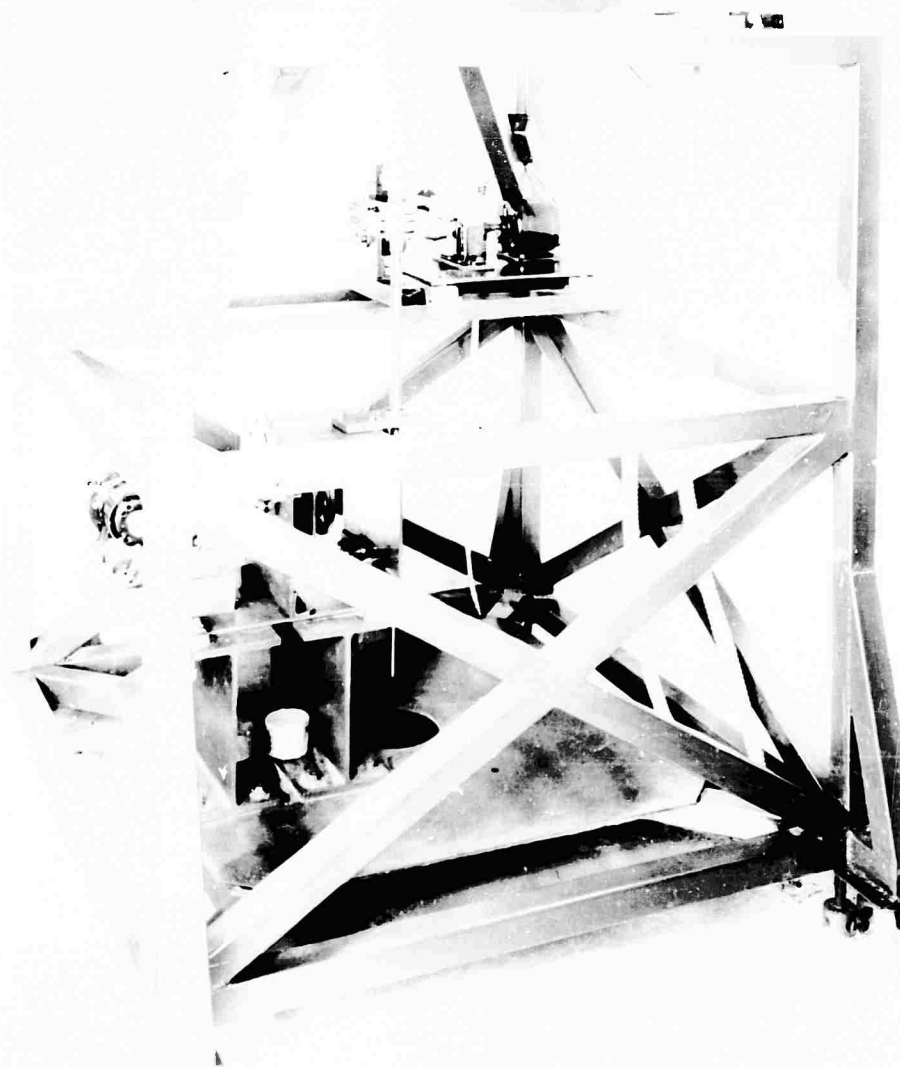Appendix I

Fig. 2 - STOCKBARGER FURNACE

Fig. 3 - SUPPORT ROD ASSEMBLY AT STOCKBARGER FURNACE.

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same for each crystal (one cm per hour), the maximum temperature has been varied from 1064° C to 1090° C, with corresponding temperature gradients of 4. 1° C/cm to 3. 7° C/cm. A number of interesting observations can be made in these systems prepared by normal freezing: (1) the top of each boule has small quantities of excess metal segregated at its periphery. These excess metal regions are thin (0. 1 mm) and are usually isolated in small islands. The shapes of these islands of excess metal are conveniently defined by re-sistance-probe mapping. (2) Those crystals which have no porosity evidence marked sublimation. As much as one third of the total charge transfers to the upper region of the quartz ampoule. And (3), crystals with a highly por-ous matrix do not sublime. These phenomena can be interpreted in light of the data presented in de Nobel's study of the CdTe system.

Figure 4 is the temperature-composition diagram of the system Cd-Te. [1] The visual method of obtaining this liquidus curve means that high resolution of detail is not possible. However, a number of speculations can be drawn from the general shape of the curve. The cusp in the liquidus curve at the maximum melting point indicates that this is not an instance of continuous solid solution formation with a maximum melting point. For the case where each component raises the freezing point of the other, the deri-vative of the liquidus curve must be continuous. For the cadmium-rich mix-tures a sharp decrease of the melting point is observed within a few percent deviation from the stoichiometric composition (53. 2 weight % Te). The pla-teau which exists out to high cadmium concentrations probably is the base of
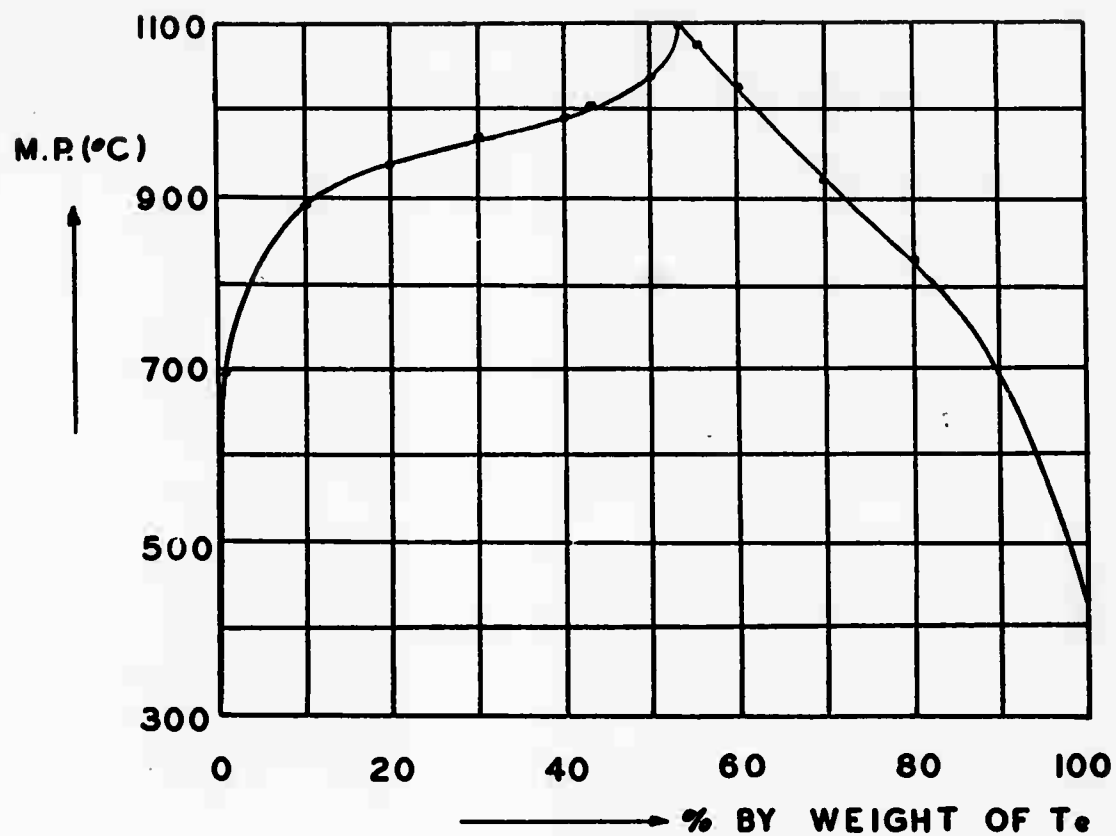
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FIG. 4. THE T-x DIAGRAM OF CdTe

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a partially miscible liquid dome. In this region, a homogeneous melt will

have a tendency to separate into two liquid phases: one with a composition

close to Cd:Te = 1:1 and one which consists mainly of pure cadmium.

Figure 5 is the temperature - composition diagram of the system

Cd-Te greatly expanded about the stoichiometric composition.[1] It is appar-

ent that stoichiometric compound melts considerably below the maximum

melting point. This portends the generation of an n-p junction in a pure melt

of overall stoichiometric composition. Lack of junction formation means

that either the melt is initially richer than 7.5×10^7 excess Te atoms/cm^3

or that other impurity doping mechanisms are dominant.

If excess cadmium or tellurium were present, relatively high

pressures of these components would be generated in the gas phase at the

melting point of CdTe. Sublimation would be minimized if the vapor consisted

mainly of Cd and Te_2. Sublimation of CdTe would then require diffusion of

both cadmium and tellurium, the diffusion rates being proportional to the

partial pressures. But if P_{Cd} is large, P_{Te_2} is small, and vice versa.

Therefore, sublimation is diminshed at large values of either P_{Cd} or P_{Te_2}.

However, when the liquid CdTe has a composition markedly different from

the solid crystallizing from it, the excess will be segregated at the solid-

liquid interface. The large vapor pressures of Cd and Te_2 (which minimize

sublimation) can then lead to gas bubble formation and a porous crystal.

Crystals of CdTe grown by the gradient technique in quartz am-

poules evidence irregular cleavage. The crystals grow with well defined
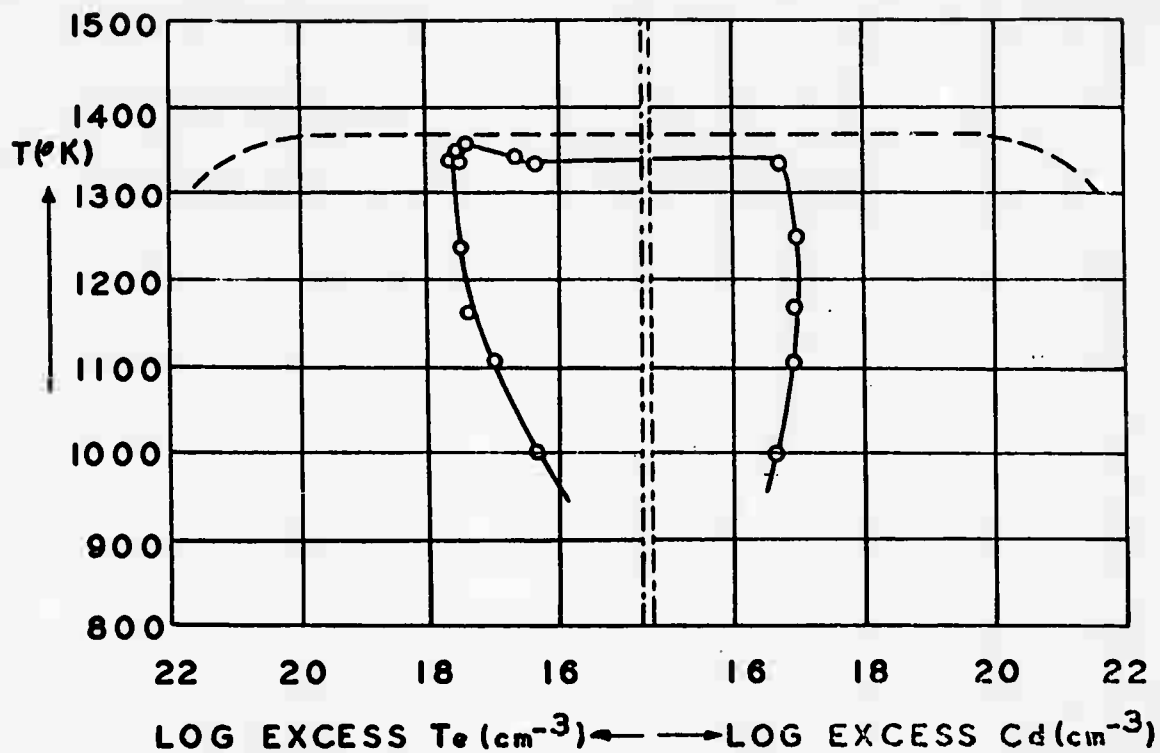
FIG.5. THE T-x DIAGRAM OF CdTe. THE SYMBOLS O
IN THE FIGURE GIVE THE CALCULATED VALUES OF
THE SOLIDUS LINE. THE LIQUIDUS IS GIVEN BY AN
ARBITRARY DASHED LINE.

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(111) twin planes and the preferred direction of growth appears to be the (111) axis. However, repeated attempts to utilize the cleavage properties of the wurzite system to section CdTe were not successful.

Thin slabs of CdTe are most conveniently obtained by sawing. A hacksaw-type frame was affixed to the blade support bar of a Spencer sliding microtome. No. 1/0 and 1/J jeweler's saw blades slice the samples cleanly at a rate of 2 to 5 microns per cut.

Sliced discs of CdTe are rough ground with 320 SiC on glass and then then fine ground with 600 SiC on glass. At this point grain boundary structure is clearly visible with low angle illumination. Low and high angle boundaries are clearly defined by their varying reflectivities. The ground surfaces can be cleaned and both the twin lines and grain boundaries delineated by a chemical etch. This consists of immersion in conc. HNO_3 at 30° C for 2 min followed by a 10% NaOH, $Na_2S_2O_4$ rinse at 60 to 70 ° C for 3 to 5 min. The specular surfaces obtained can be examined by the unaided eye for gross polycrystallinity and twinning. A microscopic examination with dark field-vertical illumination does not generally reveal additional defect structure.

The first crystals prepared in this laboratory were characterized by a high degree of distortion crystallization probably induced by the blow-holes in the matrix. As better control over stoichiometry was obtained and as the growth conditions were refined, the porosity of the crystals was reduced. This was accompanied by an increase in the size of the single crystal domains in the boules. Eventually single crystals were obtained of

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approximately one cm diameter which were completely free of any macros-
copic porosity. All of these crystals evidenced twinning to a marked degree.
Grain boundaries are, of course, not desirable since they represent potential
barriers; twins, however, do not act as potential barriers and should not
influence the electrical characteristics of the matrix.

Crystals prepared from normally stoichiometric melts have elec-
trical resistivities in the megohm-cm range. Deliberate additions of 0.01
to 0.1 mol % indium were made to the nominally stoichiometric melts. The
resultant boules showed n-type behavior and electrical resistivities from 5
ohm-cm down to < 1 ohm-cm. The boules are essentially single crystal,
have no porosity and should be well suited for carrier lifetime and mobility
measurements. These same crystals can be fabricated into photovoltaic
devices.

Appendix II

on

SOLAR CELL FABRICATION STUDIES

by

Robert J. Robinson

Appendix II

Appendix II
on

SOLAR CELL FABRICATION STUDIES

Introduction

Solar cell fabrication experiments were carried out on presently available cadmium telluride in order to evaluate it from the standpoint of solar cell application even though it was known that the material was not single crystal. In part, the purpose was to determine how the material behaved during a fabrication cycle. Samples from three ampoules were used in these experiments; the origin, nominal doping level, and approximate resistivity level of the three ampoules are shown in Table I.

Table I

SAMPLE CHARACTERISTICS

	Origin	Nominal Doping Level	Approximate Resistivity
No. 1	Semi-Elements	10^{17} In atoms	10^6 ohm-cm
No. 7-8	ARF	.01 Mol percent In	10^5 ohm-cm
No. 12	ARF	.1 Mol percent In	1 ohm-cm

Mechanical Properties

The term mechanical property is used here in the limited sense of how easily the ampoules can be sliced or cut. Two methods were used for cutting thin sections from the ampoules: a diamond saw and secondly a

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jeweler's saw mounted in a microtome. The Semi-Element's sample was very brittle and difficulty in sample preparation was found with both diamond saw and jeweler's saw. This behavior is believed to be due principally to the polycrystalline nature of the ampoule.

The ampoule which was most easily cut was the one which was the least polycrystalline, ARF No. 7-8, and moreover, this ampoule showed little porosity due to "blowholes". For this reason it is believed that when dense, single crystal ampoules become available slicing will cease being a problem even though inherently cadmium telluride may be more brittle than germanium or silicon.

While the two methods of slicing the currently available ampoules cannot be directly evaluated since different personnel were involved in the actual operations, it appears that the jeweler's saw in the microtome leads to better slices and less waste of material.

Diffusion Experiments

From macroscopic thermoelectric measurements each of the three ampoules was found to be n-type so that diffusion of an acceptor material or heating in vacuum to form cadmium vacancies which act as acceptors was indicated to form a p-n junction. Earlier experiments on a few small single crystals which were not purposely doped showed that short time radiant heating in vacuum did lead to a p-type skin, as determined by thermoelectric measurements. These experiments were repeated with these larger samples.

In doping experiments, silver was used as the added impurity acceptor. The silver was prepared for the samples in three different ways: 1) silver nitrate solution was placed on the sample and allowed to dry; this leads to a metallic-appearing precipitate on the n-type cadmium telluride; 2) silver was evaporated on to one face of the sample, and 3) the samples were heated in the presence of silver. In each of these cases the samples were heated in a radiant furnace mounted inside of an evacuated bell jar. For case number 3 above, the sample and silver were placed inside a silica tube which was plugged with asbestos. The silica tube was then placed inside of the radiant heater. Other diffusion experiments were carried out of the double diffusion type. Indium metal, a donor, was placed on one side of the sample and evaporated silver on the other side; then double diffusion was attempted at various temperatures.

The experiments were carried out at different temperatures ranging from 700 degrees centigrade to 200 degrees centigrade, and from times varying between 5 minutes at the higher temperatures to 12 hours at 200 degrees centigrade. However, most of the experiments were carried out at 550 degrees centigrade for various heating times.

A number of conclusions can be drawn from these experiments. First, there is a strong tendency for pitting at temperatures above 200 degrees centigrade, which results most likely from non-uniform evaporation of cadmium telluride. Secondly, the photovoltaic response of the samples is very small. In fact, higher open circuit photovoltages were found by probe

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methods, on untreated samples. Thirdly, the silver nitrate treatment leads to the most rapid silver diffusion; in fact, there are indications that silver bridges shorted out some samples after heating, presumably due to silver bridging at grain boundaries.

These experiments were preliminary in nature, and the poor results noted in the photovoltaic response led to a series of experiments using a thermoelectric probe device which will be discussed in another appendix. The thermoelectric probe measurements show, however, that microscopically the samples consist of alternating n and p-type regions. It is believed that this leads to a compensation cancelling or shorting of the photovoltaic emf. Further, the pitting of the samples arising from non-uniform evaporation from the surface could also be explained on the basis of the inhomogeneities indicated by the n and p-type regions on the surface. Strong pitting appears to be associated with a p-type thermoelectric effect.

Backing Electrodes

A strong mechanical bond to a backing electrode of copper or sheet steel was found by indium soldering the sample, and alloying common solder on the backing sheet to the indium solder on the sample. If done properly this leads to a bond even for the Semi-Element's sample which had very little mechanical strength of itself after the heating experiments.

Chemical Junction Experiment

A p-type layer was placed on a macroscopically n-type sample by dipping the sample into nitric acid; the existence of the p-type layer was proved

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using a thermoelectric probe measurement, but the sample showed only a negligible photovoltaic effect. This was a preliminary experiment and it is not known to what depth the layer was formed. Further experiments along this line are planned as a method of avoiding the heating associated with the diffusion method.

Appendix III

on

THERMOELECTRIC PROBE MEASUREMENTS

by

Robert J. Robinson

THERMOELECTRIC PROBE MEASUREMENTS

Introduction

The solar cell fabrication experiments described in the previous appendix led to two conclusions which suggested marked inhomogeneity in the samples. The first of these was the strong tendency to pit during the heating cycle in the diffusion experiments. The second was the lack of photovoltaic response over a wide area but a definite photovoltaic response to previous probe measurements. It was decided, therefore, to make a device which would permit small area probing for n and p-type regions. A soldering iron with a micro tiplet was mounted in a traveling microscope, and the generated thermal emf was detected with a Hewlett-Packard Model 425A DC Micro Volt Ammeter.

The anticipated inhomogeneities were found as indicated by alternate n and p regions across the sample. The measurements were made on slices from the different ampoules and not the ampoule itself. The faces which were probed were approximately perpendicular to the growth direction of the ampoule. For these measurements the junctions between the n and p region were parallel to the growth direction.

Measurements Following Diffusion Experiments

A profile thermoelectric probe measurement was made across a sample which had been heated in vacuum to 650 degrees centigrade for 30

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minutes. This sample showed pitting after heat treating and the probe profile was arranged to pass through one of these pits. The data presented in Figure 1 is the result of the measurement. It is representative of the data taken on vacuum heated samples.

In the next graph, Figure 2, a profile is shown for a sample which had been heated to 550 degrees centigrade after a light silver evaporation on the surface. Again pitting occurred and this region of pitting was p-type. The fact that most of the sample is n-type, even though silver presumably had diffused in, is not understood. However, the amount of evaporated cadmium telluride from the sample may have precluded much silver diffusion. It may well be that the silver diffused in non-uniformly.

The next profile attempted to check this point. A sample which had been heat treated following silver evaporation was measured but this time the profile was taken over a region showing little pitting. In Figure 3 it is seen that the sample is strongly p-type in certain regions as evidenced by the small thermoelectric voltage; however, there was no obvious pitting in this region. There appears to be evidence here for non-uniform diffusion of silver. Other samples from the same ampoule show n and p-type regions without any heat treatment, but the thermoelectric voltages are much higher indicating a far smaller number of holes than are shown in Figure 3.

A profiles of a sample which has not been heat treated in any way is shown in Figure 4. It is obvious that a large number of p-n junctions are involved but the large positive thermoelectric voltages indicate a far smaller
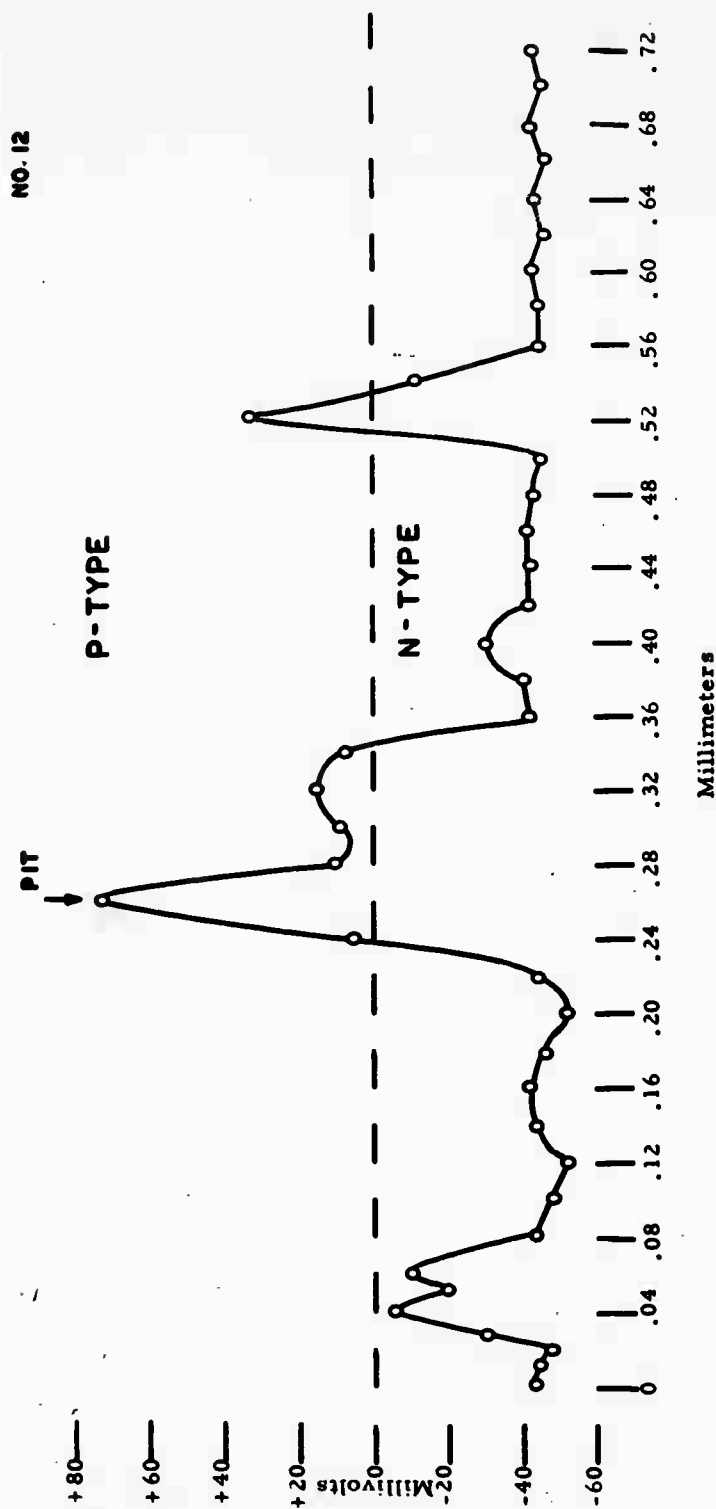
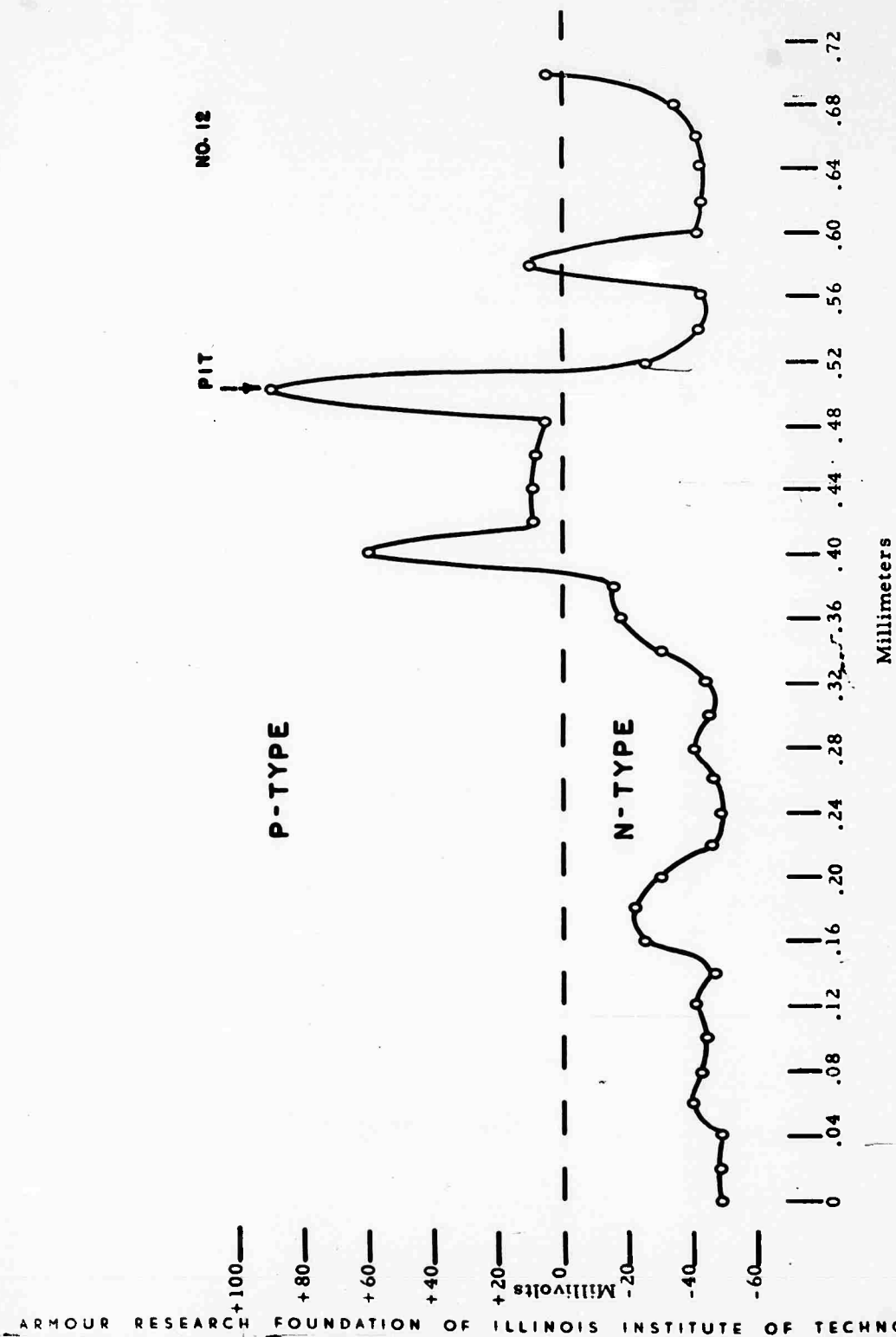Fig. 1 - VACUUM HEATED SAMPLE SHOWING PITTING

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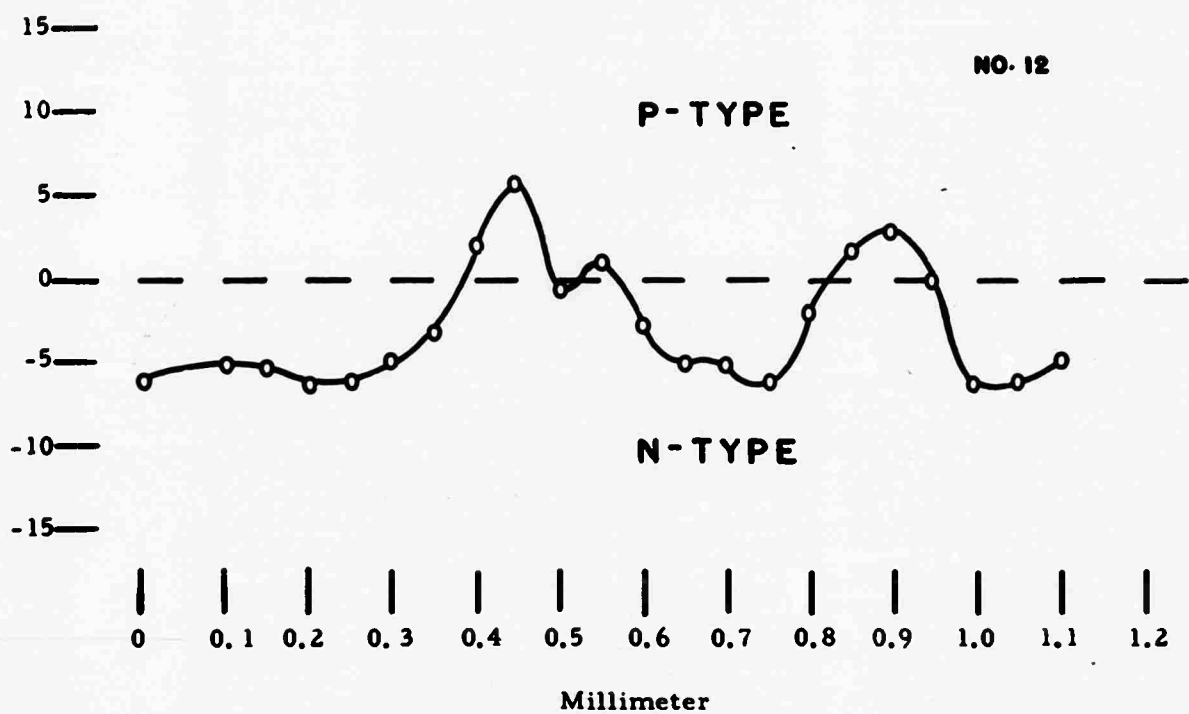Fig. 2 - HEAT TREATED SAMPLE FOLLOWING SILVER VAPOR DEPOSITION.

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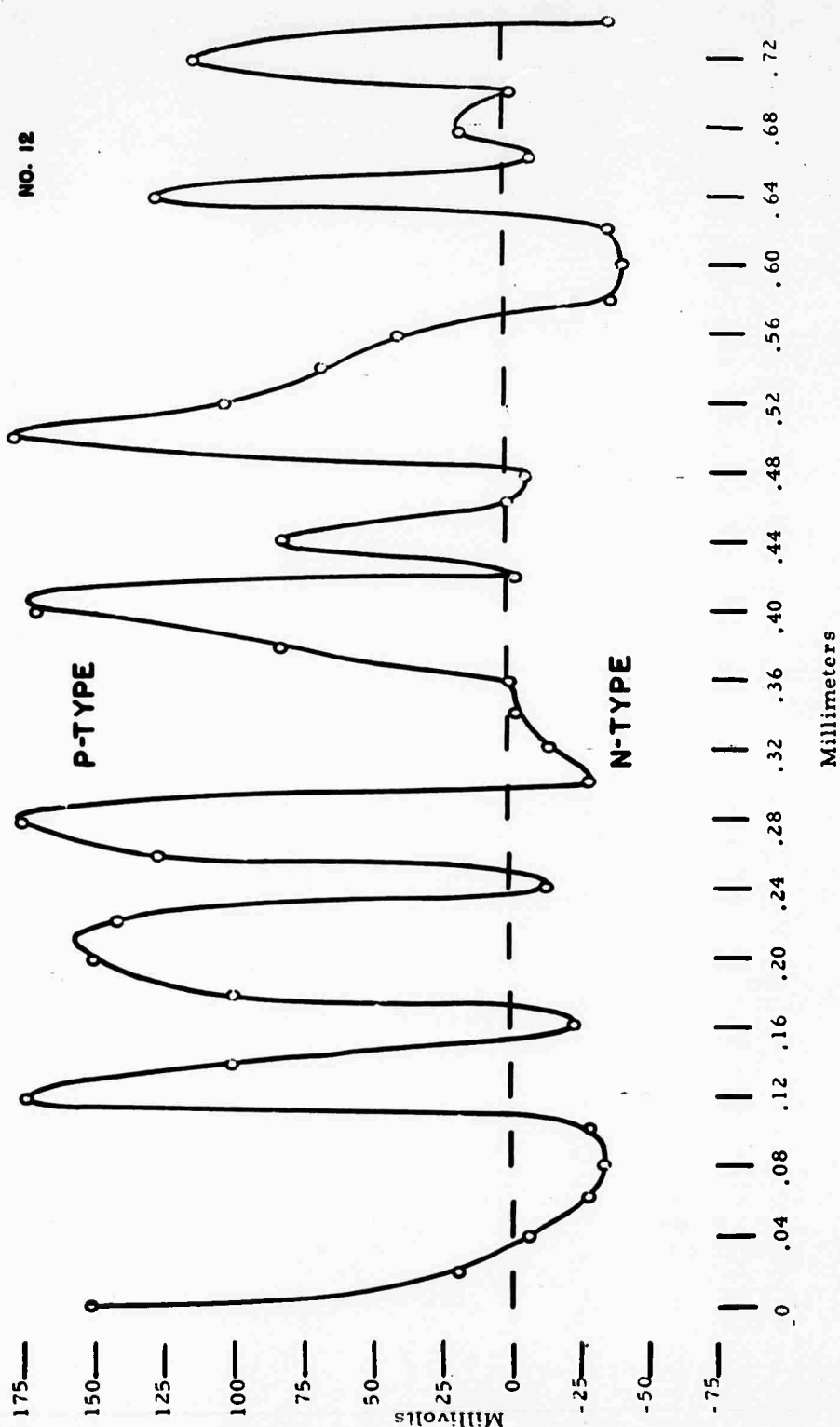Fig. 3 - HEAT TREATED SAMPLE NO PITTING IN THIS PROFILE.

Fig. 4 - UNTREATED SAMPLE NO. 12

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number of holes than are shown in Figure 3.

The last curve, Figure 5, shows a profile of untreated material from ampoule No. 7-8. Again it is seen that the sample is inhomogeneous. A strong argument for zone refining of cadmium telluride can be made just based on curves of the sort discussed in this appendix.

Very recently a new ampoule grown at Armour Research Foundation has become available. Preliminary results with the thermoelectric probe measurement device indicate that the material is always n-type, and probe photovoltaic measurements give open circuit photovoltages of 0. 6 volt. A marked improvement in crystal growth is indicated.
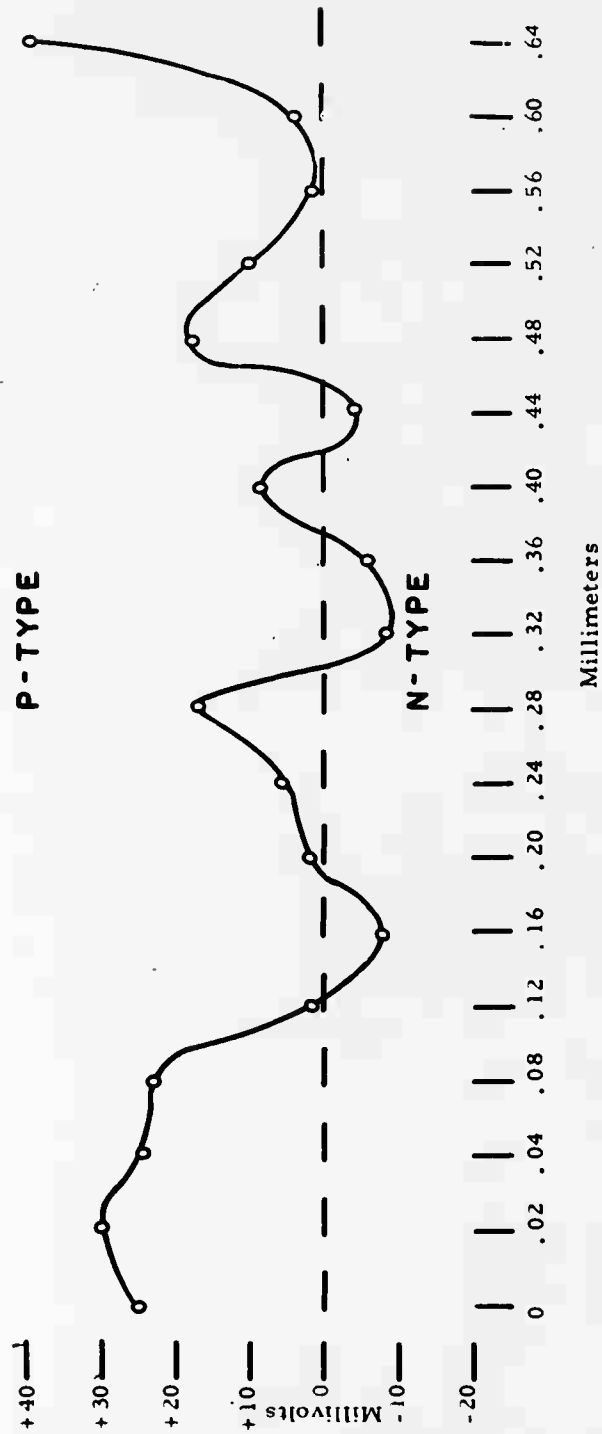
Fig. 5 - UNTREATED SAMPLE NO. 7 - 8

Appendix III